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Enhancement of spontaneous polarization in lead zirconate titanate thin films by Dy^{3+} substitution

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Spontaneous polarization can be enhanced by increasing the crystal anisotropy of tetragonal $Pb(Zr,Ti)O_3$ [PZT] lattice by Zr and Ti-site substitution with Dy^{3+} cations. Spontaneous polarization (P_s) in epitaxial film of 2% Dy^{3+}-substituted tetragonal $Pb(Zr_{0.40}Ti_{0.60})O_3$ [Dy–PZT] was compared with that of nonsubstituted $Pb(Zr_{0.40}Ti_{0.60})O_3$ [PZT] to investigate intrinsic contribution of the Dy^{3+} substituion to the P_s improvement. Epitaxial thin films of PZT and Dy–PZT with (111) orientations were grown on $(111)_cSrRuO_3//(111)Pt//(100)YSZ//(100)Si$ substrates by chemical solution deposition. The saturated polarization values of PZT and Dy-PZT films with (111) orientation were 41 and 48 $\mu C/cm^2$, respectively. The estimated P_s values of PZT and Dy–PZT films from the saturation polarization values were 71 and 84 $\mu C/cm^2$, respectively. The P_s value of this PZT was in good agreement with previous reports. The increase in P_s of the epitaxial Dy^{3+}-substituted PZT film is attributed to the enhancement of the crystal anisotropy, i.e., tetragonality, of the tetragonal PZT lattice. This shows that the enhancement of the ferroelectricity of the tetragonal PZT films can be achieved by ion substitution, just as it can in $Bi_4Ti_3O_{12}$-based film. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2125123]

Tetragonal lead zirconate titanate $[Pb(Zr,Ti)O_3]$ (PZT) thin films have attracted much interest for nonvolatile memory (NvRAM) application and microelectromechanical systems, due to their excellent ferroelectric and piezoelectric properties, respectively. Further improvement of the ferroelectric properties of $Pb(Zr,Ti)O_3$-based thin films is required for the integration of high-density NvRAM to get a large sensing margin of small capacitor cells.[1] Ion substitution is widely investigated to enhance the ferroelectricity of $Pb(Zr,Ti)O_3$ and thin films of $Bi_4Ti_3O_{12}$-based materials. For bulk $Pb(Zr,Ti)O_3$, ion substitution for enhancing the polarization has been widely investigated, but the best substituent ion and an effective substitution strategy of $Pb(Zr,Ti)O_3$ films has not been discovered yet.[2–5] In previous studies, the main idea was to have lanthanide elements such as La^{3+} and Nd^{3+} occupy Pb sites, or higher valence elements such as Nb^{5+} occupy the Zr and Ti sites. For example, Bolten *et al.*[3] reported that Nd^{3+}-substituted tetragonal $Pb(Zr,Ti)O_3$ film degraded the remanent polarization (P_r) of PZT film because it decreased the crystal anisotropy, i.e., the ratio of lattice parameter of c to a, (c/a ratio), in $Pb(Zr,Ti)O_3$ crystals. On the other hand, there was hardly any report on the ferroelectric properties of $Pb(Zr,Ti)O_3$ substituted by smaller lanthanide ions. Park *et al.* and Majumber *et al.* reported the preferred B-site occupancy of particular lanthanide elements such as Gd^{3+}, Dy^{3+} and Yb^{3+} in Pb-based perovskite ABO_3.[6,7] The present authors recently revealed that the ferroelectric properties of tetragonal $Pb(Zr,Ti)O_3$ film can be improved by Zr- and Ti-site substitution by lanthanoid ions.[8] In particular, $PbDy_{0.02}(Zr_{0.40}Ti_{0.60})_{0.99}O_3$ was found to increase the P_r value from 20 to 25 $\mu C/cm^2$ for (111)-preferred-oriented polycrystalline $Pb(Zr_{0.40}Ti_{0.60})O_3$ [PZT] films prepared by chemical solution deposition (CSD).[8] This improvement is due to the enhancement of the c/a ratio of the tetragonal PZT. To clarify whether intrinsic ferroelectricity is enhanced by Dy^{3+} substitution or not, the ferroelectric properties should be investigated using epitaxial film because not only the intrinsic substitution but also the effects of extrinsic parameters, such as the film destiny, the degree of the crystallinity, and the distribution of the crystal orientation, contribute to the ferroelectricity of the polycrystalline PZT film.[9] In this letter, (111)-oriented epitaxial tetragonal PZT films were grown on $(111)SrRuO_3//(111)Pt//(100)YSZ//(100)Si$ substrates. The (111)-orientated PZT film is suitable for estimating the spontaneous polarization (P_s) value because there is no contribution from 90° domain switching

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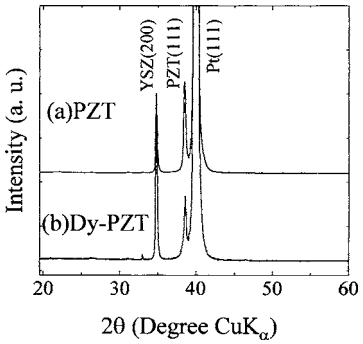

FIG. 1. XRD patterns of (a) nonsubstituted PZT and (b) Dy^{3+}-substitution PZT films deposited on (111)$SrRuO_3$//(111)Pt//(100)YSZ//(100)Si substrates.

like there is for other orientations, such as (100)/(001) and (110)/(101)-oriented PZT films. The P_s values of Dy-substituted and nonsubstituted PZT were estimated using these (111)-oriented epitaxially grown films to confirm the enhancement of the P_s value.

Epitaxial thin films with 400 nm in thickness were fabricated on (111)$SrRuO_3$//(111)Pt//(100)YSZ//(100)Si substrates (YSZ: yttria-stabilized zirconia) by CSD. The (111)-oriented $SrRuO_3$ films were grown by metalorganic chemical vapor deposition (MOCVD) on (111)Pt//(100)YSZ//(100)Si substrates.[10] Trihydrated lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$), titanium normal-butoxide ($Ti(O \cdot n\text{-}C_4H_5)_4$), zirconium iso-propoxide ($Zr(O \cdot i\text{-}C_3H_7)_4$), dysprosium nitrate $Dy(NO_3)_3$ and 2-methoxyethanol were the starting materials for the preparation of CSD precursor solutions. The nominal compositions of the precursor solutions were controlled to be $Pb_{1.00}(Zr_{0.40}Ti_{0.60})O_3$ [PZT] and $Pb_{1.00}Dy_{0.02}(Zr_{0.40}Ti_{0.60})_{0.99}O_3$ [Dy-PZT] with 5% Pb excess. The optimum Dy content was already determined to be 2% in the previous study.[8] The concentration of the precursor solutions was controlled to be about 0.24 mol/dm^3. The solutions were spin coated at a rotation rate of 3000 rpm. A sequence comprising spin coating, drying at 150 °C for 10 s, and pyrolysis at 400 °C for 3 min was performed several times to deposit a film. Finally, the samples were fired at 650 °C for 5 min in air for crystallization.

The constituent phase and crystal orientation of the films were confirmed by x-ray diffraction (XRD) using a Rigaku RINT 2100 x-ray differctometer with Cu $K\alpha$ radiation. Pole figure measurements of the films were performed by x-ray diffraction (XRD) using a Philips MRD. The surface morphology and film thickness of the thin films were observed with a Hitachi S4500 scanning electron microscope together with atomic force microscopy (AFM). The polarization (P) -electric field (E) hysteresis curve up to 380 kV/cm (14 V) was examined using a Toyo Corporation FCE ferroelectric test system. The leakage current densities were measured using a Hewlett–Packard 4155B in 0.1 V steps with a waiting time of 0.2 s between each step. To evaluate the ferroelectric properties, circular Au top electrodes with a diameter of about ~500 μm were deposited by vacuum evaporation deposition through a metal mask.

Ions of 2% Dy^{3+} were confirmed to occupy the Zr and Ti sites of PZT films preferentially by the Raman measurement.[11] Figure 1 shows $2\theta-\omega$ XRD patterns of PZT and Dy-PZT films. Both films consisted of the tetragonal PZT perovskite phase with the preferred PZT (111) orientation to the substrate surface. These films contained no secondary phases, such as the pyrochlore phase ($Pb_2Ti_2O_7$) or Dy_2O_3 phase.

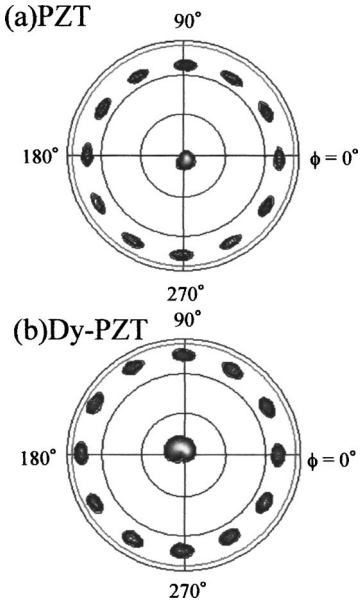

FIG. 2. X-ray pole figures measured at the fixed 2θ angel of about 38.1 ° corresponding to PZT(111) for (a) nonsubstituted PZT and (b) Dy^{3+}-substitution PZT films.

Figures 2(a) and 2(b) show x-ray pole figures measured at the fixed 2θ angle of about 38.1°, which corresponds to the PZT (111) for the PZT and Dy-PZT films shown in Fig. 1. Twelve spots ascribed to the PZT(111) orientation were observed at around $\varphi=70.5°$ together with the center one for both films. These results indicate that these films were epitaxially grown on the substrates. These spots are caused by four domains of PZT crystal with different in-plane orientations that have three symmetric rotational PZT(111) diffractions of about $\varphi=70.5°$. The in-plane orientations of (111)PZT domains are consistent with those of (111)$SrRuO_3$ and (111)Pt domains.[12] These orientations due to the epitaxial growth of (111)PZT on each (111)$SrRuO_3$ have been already discussed in previous work.[10,12] These results confirm the epitaxial growth of PZT films on the substrates by CSD as well as by MOCVD.[9,12,13] Obvious grain structure was not detected for both films and no obvious change in microstructure was detected by the AFM observations.

Figure 3 shows P-E hysterisis loops measured at a frequency of 1 kHz for the PZT and the Dy–PZT films. Well-saturated hysteresis loops were observed for both films. Figure 4 shows the saturation properties of P_r and coercive field (E_c) values for the PZT and Dy–PZT films shown in Fig. 3. The P_r and E_c values abruptly increased at about 100 kV/cm, and well-saturated P_r and E_c values were observed against the maximum electric field. The P_r and E_c values of the Dy–PZT film at the maximum electric field of 380 kV/cm were measured to be 40 μC/cm^2 and 88 kV/cm, while those of the PZT film were 35 μC/cm^2 and 85 kV/cm, respectively. The saturated polarization (P_{sat}) values of the PZT and Dy–PZT films evaluated from tangent lines of the hysteresis loops in Fig. 3 at the maximum electric field of 380 kV/cm are 41 and 48 μC/cm^2, respectively. The ratio of the P_{sat} along PZT $\langle 111 \rangle$ to P_s along the polar PZT $\langle 001 \rangle$ was estimated to be 57% because the polar axis

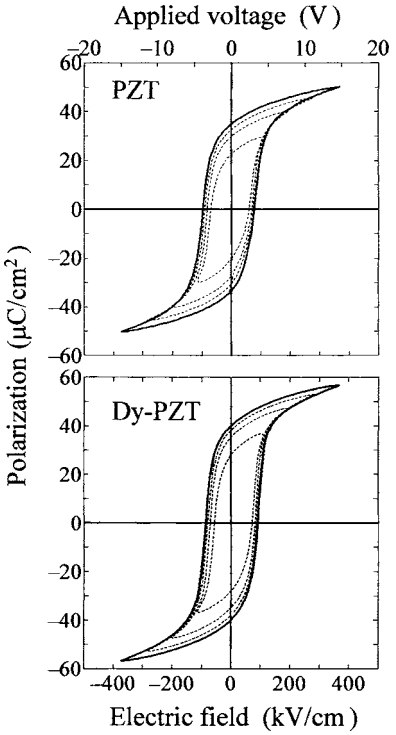

FIG. 3. *P-E* hysterisis loops measured at 1 kHz for (a) nonsubstituted PZT and (b) Dy^{3+}-substitution PZT films.

inclines about 55° from normal of the film surface for epitaxial (111)-oriented PZT film. The extrapolation using this relationship gives P_s values along the polar axis of 71 and 84 $\mu C/cm^2$ for the PZT and Dy–PZT crystal, respectively. Using a 100% *c*-axis-oriented epitaxial PZT film, Morioka *et al.*[13] estimated the P_s values of nonsubstituted PZT crystal (Zr/Ti=40/60) to be approximately 75 $\mu C/cm^2$, which is consistent with the present result.[13] This shows that the quality of the present epitaxially grown film prepared by CSD is sufficient for estimating the P_s value accurately. The present results clearly show that the P_s value of Dy-PZT film is significantly larger than that of nonsubstituted PZT.

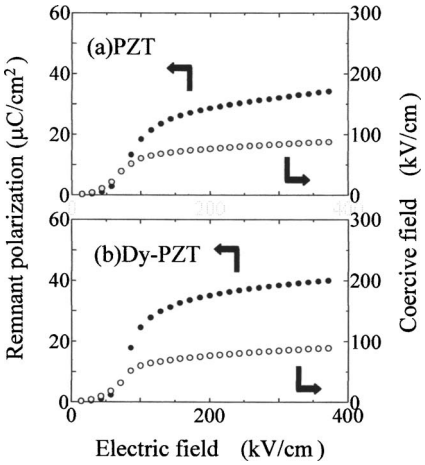

FIG. 4. Saturation properties in remanent polarization (P_r) and coercive field (E_c) for (a) nonsubstituted PZT and (b) Dy^{3+}-substitution PZT films.

The *c*/*a* ratio of the film was estimated from PZT 200 and 002 peaks on $2\theta-\omega$ scan at the fixed Psi angle of about 54.7 ° corresponding to (100)/(001) orientation of the film with (111) surface normal orientation. The *c*/*a* ratios of PZT and Dy–PZT films at room temperature were estimated to be 1.040 and 1.046, respectively. Additionally, the Curie temperature of polycrystalline PZT and 2%-Dy^{3+}-substituted-PZT films deposited on $Pt/TiO_2/SiO_2/(100)Si$ substrates was ascertained to be almost 410 and 430 °C, respectively, by the high-temperature x-ray analysis. In PZT-based materials, increase of T_c responds to the increase of the *c*/*a* ratio of tetragonal PZT at room temperature. This *c*/*a* ratio induced the increase of P_s as Morioka *et al.* pointed out.[13] The increase of the present *c*/*a* ratio by 2% Dy substitution can be estimated to be response to the 7 $\mu C/cm^2$ increase in P_s based on the equation proposed by Morioka *et al.* for tetragonal PZT film.[13] The present result demonstrates that the ferroelecticity of tetragonal PZT films is enhanced by ion substitution, just as it is in Nd-substituted $Bi_4Ti_3O_{12}$-based films.[14]

In summary, P_s values of nonsubstituted PZT and Dy–PZT were estimated using the (111)-oriented epitaxial thin films grown on $(111)SrRuO_3//(111)Pt//(100)YSZ//(100)Si$ substrates by chemical solution deposition. These films had crystal orientation of (111) PZT and were epitaxially grown on the substrates. The P_{sat} values of the PZT and Dy–PZT films were 41 $\mu C/cm^2$ and 48, respectively. The P_s value estimated from these P_{sat} of Dy–PZT film was 84 $\mu C/cm^2$, which is significantly larger than that of nonsubstituted PZT (71 $\mu C/cm^2$). The polarization enhancement in PZT film due to the increase of crystal anisotropy was achieved by the Dy^{3+} substitution.

[1] J. F. Scott and C. A. P. de Araujo, Science **246**, 1400 (1989).
[2] S. Majumder, B. Roy, R. Katiyar, and S. Krupandhi, Appl. Phys. Lett. **79**, 239 (2001).
[3] D. Bolten, U. Bottger, T. Schneller, M. Grossmann, O. Lohse, and R. Waser, Integr. Ferroelectr. **32**, 93 (2001).
[4] C. Barlingay and S. Day, Appl. Phys. Lett. **61**, 1278 (1992).
[5] S. Yoon, H. Kang, S. Kucheike, H. Kim, and H. Jung, J. Am. Ceram. Soc. **81**, 2473 (1998).
[6] H. B. Park, C. Y. Park, Y. S. Hong, K. Kim, and S. J. Kim, J. Am. Ceram. Soc. **82**, 94 (1999).
[7] S. B. Majumder, P. S. Dobal, B. Roy, S. Bhasker, and R. S. Katiyar, Ferroelectr., Lett. Sect. **28**, 85 (2001).
[8] H. Nakaki, H. Uchida, S. Yokoyama, H. Funakubo, and S. Koda, Jpn. J. Appl. Phys., Part 1 **43**, 6558 (2004).
[9] C. Foster, G. Bai, R. Csencsits, J. Vetrone, R. Jammy, L. Wills, E. Carr, and J. Amano, J. Appl. Phys. **81**, 2349 (1997).
[10] S. Okamoto, T. Watanabe, K. Akiyama, S. Kaneko, H. Funakubo, and S. Horita, Jpn. J. Appl. Phys., Part 1, **44**, 5102 (2005).
[11] H. Nakaki, H. Uchida, K. Nishida, M. Osada, H. Funakubo, T. Katoda, and S. Koda, Jpn. J. Appl. Phys., Part 1 **44**, 6905 (2005).
[12] Y. Kim, H. Morioka, S. Okamoto, T. Watanabe, S. Yokoyama, A. Sumi, H. Funakubo, and K. Saito, Appl. Phys. Lett. **86**, 212905 (2005).
[13] H. Morioka, S. Yokoyama, T. Oikawa, and H. Funakubo, Appl. Phys. Lett. **85**, 3516 (2004).
[14] T. Kojima, T. Sakai, T. Watanabe, K. Saito, M. Osada, and H. Funakubo, Appl. Phys. Lett. **80**, 2746 (2002).